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# Some Comments on Scattering Phenomena

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It is well known that in the calculation of wave functions very good results can be obtained for the molecular or atomic energy, namely 99 % of the experimental value or better. Some other physical properties do not agree as well with experimental data; these include dissociation energies and ionization potentials. In the case of the physical properties dependent for their calculation upon electron charge densities a better agreement is obtained, perhaps because the first order correction to the Hartree–Fock charge distribution is zero. The good agreement obtained for total energies may come from compensated errors in various parts of their distributions, and cannot give sufficient information concerning the other properties. It is now reasonable to believe that very accurate calculations and experiments on scattering phenomena may be used together to study electronic distribution in various scatterers. It is the aim of this paper to show that scattered intensities and spectral studies of the modified radiation may give complementary information.

Several calculations made for light atoms and molecules are discussed and compared with experimental data when possible. Some results obtained are discussed in relation to chemical bonding for which accurate atomic and molecular electronic densities are required.

## Introduction

During recent years a large number of calculations have been done on scattering factors and intensities and on the shape of the Compton profiles. Generally made by different authors, these calculations have never been definitely compared. This comparison now seems very useful with the advent of high resolution spectrometers and more accurate wave functions. It is only recently that Kilby (1965) has shown that the Compton profile, to a first approximation, can be deduced from the Waller & Hartree (1929) theory; when the results obtained with the help of this theory are compared with experimental data, it is shown that the method is very convenient for studying the effects of scattering as well as the Compton profiles. Although these methods are first approximations to more rigorous theories, they give good results as far as incident beams of high energy are concerned.

Important contributions to this work have recently been published particularly by Bonham & Iijima (1963), Bonham (1965*a*,*b*,*c*,*d*,*e*); Tavard, Roux & Cornille (1962, 1963), Tavard, Roux & Rouault (1964), Tavard & Roux (1965); Tavard (1966); Kilby (1963, 1965), and Bartell & Gavin (1964). Important sets of references can be found in these articles.

## Waller and Hartree's theory

It is easy to show with the use of Waller & Hartree's theory that scattered intensities, in the case of incident X-ray of high energy, can be written as a sum of terms in the form:

$$I_{0m} = I_{cl} \left| \frac{\nu'}{\nu} \right|^3 |D_{0m}|^2 \qquad (1)$$

where $\nu$ and $\nu'$ are the frequencies of the incident and scattered radiations, and

$$D_{0m}=\int \psi_0(\mathbf{x})\left[\sum_{j=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_j}\right]\psi_m(\mathbf{x})\mathbf{dx}. \qquad (2)$$

In equation (2) $\psi_0$ is the wave function for the ground state of the scatterer; $\psi_m$ is the wave function of an excited state $m$ which could be in the discrete or continuous spectrum of the system; $\mathbf{q}$ is the usual parameter related to the diffraction angle

$$|\mathbf{q}|=4\pi\frac{\sin\theta/2}{\lambda} \qquad (3)$$

with $\lambda$ the wave length of the incident radiation and $\theta$ the scattering angle between the incident and scattered rays. $I_{cl}$ is the Thomson expression related to the intensity scattered by an electron. The $\mathbf{x}$ values are the space and spin coordinates for the $N$ electrons of the system.

Introducing certain approximations limiting the applicability of the formula to the case of an incident beam of high energy, the use of perturbation theory and the closure properties of the spherical harmonics, the total and coherent intensities may be written (Waller & Hartree, 1929):

$$I_{\text{tot}}=I_{cl}\int|\psi_0(\mathbf{x})|^2\left|\sum_{j=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_j}\right|^2\mathbf{dx} \qquad (4)$$

$$I_{\text{coh}}=I_{cl}\left|\int|\psi_0(\mathbf{x})|^2\sum_{j=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_j}\,\mathbf{dx}\right|^2; \qquad (5)$$

in these expressions $\nu'$ is considered not very different from $\nu$ and the ratio $\nu'/\nu$ is 1. These equations show that the only wave function required for this approximation is that of the ground state of the scatterer. The neglected terms in the Waller & Hartree theory were evaluated by Bonham (1965*a*) and are of the order of $10^{-4}$ for X-rays of 0·712 Å (Mo $K\alpha$).

If we use the usual wave functions built up with a set of orthogonalized spin orbitals $\Phi_i$ it is possible to define the structure factors by the two following expressions.

$$f(\Phi_i)=\int\Phi_i(\mathbf{x})\Phi_j^*(\mathbf{x})e^{i\mathbf{q}\cdot\mathbf{r}}\,\mathbf{dx} \qquad (6)$$

$$f(\Phi_i\Phi_j)=\int\Phi_i(\mathbf{x})\Phi_j^*(\mathbf{x})e^{i\mathbf{q}\cdot\mathbf{r}}\,\mathbf{dx} \qquad (7)$$

where $i$ and $j$ are the subscripts for the spin orbitals.

We also define the total scattering factor for the $N$ electrons of the system as

$$f=\sum_i f(\Phi_i)\,. \qquad (8)$$

Using these various expressions we can rewrite the intensities as

$$I_{\text{tot}}^{\text{R.X.}}=I_{cl}[N+\sum_{i\neq j}(f(\Phi_i)f^*(\Phi_j)-|f(\Phi_i\Phi_j)|^2)] \qquad (9)$$

and

$$I_{\text{coh}}=I_{cl}[|\sum_{j=1}^{N} f(\Phi_j)|^2]\,. \qquad (10)$$

With the use of these expressions established for the case of an incident beam of X-rays, Morse (1932), Cornille (1963), and Iijima, Bonham & Ando (1963) have shown that the same theory can be applied to the case of an incident beam of fast electrons; for example Cornille (1963) in the case of an atom gives the following equations for the elastic and total intensities:

$$I_{\text{tot}}^{\text{E.D.}}=I/q^4[Z^2-Z\sum_{j=1}^{N}(f(\Phi_j)+f^*(\Phi_j))+N+\sum_{i\neq j}f(\Phi_i)f^*(\Phi_j)-\sum_{i\neq j}|f(\Phi_i\Phi_j)|^2] \qquad (11)$$

$$I_{\text{elast}}=I/q^4[|Z-\sum_{j=1}^{N} f(\Phi_j)|^2]\,, \qquad (12)$$

where $q$ is defined as in equation (3) and $I$ is related to experimental conditions. The neglected terms were evaluated by Bonham (1965*a*) and Tavard (1966) and are of the order of $10^{-4}$ for 40-keV electrons. The functions $f(\Phi)$ are the same for both X-ray and fast-electron scattering. Examinations of equations (9), (10), (11) and (12) show that the scattering of X-rays and fast electrons can be handled by very similar formalism; if we notice that the wave functions introduced in the formulae can be atomic or molecular, we have a very useful tool for studying scattering effects.

Applying this first and approximate stage of the theory, we can get quite good results certainly in the case of light atoms and molecules for, as was demonstrated by Bonham (1965*a*, *b*, *c*), the omitted improvements are not important in these cases.

Another point of interest related to the diffraction effects is the study of the velocity distribution of the electrons of the scatterer. This could be achieved by calculation of the shape and width of the Compton profile which corresponds to transitions from the ground state of the system to the excited states situated in the continuum. This effect can be expressed by a special type of equation (2), where we suppose that the $m$ excited state is well approximated by a plane wave.

Kilby (1963, 1965) has recently shown that, with some strict conditions concerning the energy, it is possible to apply the Waller & Hartree theory to the study of the Compton profiles using a special $D_{0m}$ term, and that it is then possible to get exactly the same expression as was obtained by DuMond (1933) who considered the momentum distribution as given by

$$J(q')=\tfrac{1}{2}\int_{q'}^{\infty}\frac{I(p)}{p}\,dp \qquad (13)$$

in which $q'$ is defined by

$$q'=\frac{cl}{2\lambda_i\sin\dfrac{\theta}{2}}, \qquad (14)$$

where $\lambda_i$ is the wave length of the incident beam and $l$ is measured from the center of the Compton profile,

$\theta$ is the diffraction angle, $c$ is the velocity of light. $I(p)$ is the momentum distribution given by

$$I(p)=\int x(\mathbf{p})\gamma^*(\mathbf{p})p^2 d\Omega_p \,. \tag{15}$$

In this equation the $x(\mathbf{p})$ is the Dirac transform of the spin orbital used in coordinate space:

$$x(\mathbf{p})=(2\pi)^{-3/2}\int \Phi(\mathbf{r})e^{-i\mathbf{p}\cdot\mathbf{r}}\,\mathbf{dr} \tag{16}$$

Accurate calculations of the scattered intensities and Compton profiles are very useful, for it may be demonstrated that they provide valuable information about potential and kinetic energies. Bonham (1965) and Tavard & Roux (1965) have obtained the following expressions:

$$\left\langle \psi \left| \sum_{i<j}\sum \frac{1}{r_{ij}} \right| \psi \right\rangle = \frac{1}{4\pi^2}\int \frac{\mathbf{dq}}{q^2}|\psi|^2 \left[ \left| \sum_{j=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_j} \right|^2 - N \right] \mathbf{dx} \tag{17}$$

for the value of electronic potential energy and

$$\left\langle \psi \left| \sum_{\mu<\nu}\sum \frac{Z_\mu Z_\nu}{r_{\mu\nu}} - \sum_{\mu}\sum_{i} \frac{Z_\mu}{r_{\mu i}} + \sum_{i<j}\sum \frac{1}{r_{ij}} \right| \psi \right\rangle = \frac{1}{4\pi^2}\int \frac{d\mathbf{q}}{q^2}|\psi|^2 \left[ \left| \sum_{\mu} Z_\mu e^{i\mathbf{q}\cdot\mathbf{r}_\mu} - \sum_{i=1}^{N} e^{i\mathbf{s}\cdot\mathbf{r}_i} \right|^2 - \sum_{\mu} Z_\mu^2 - N \right] \mathbf{dx} \tag{18}$$

for the total potential energy.

It is also possible to derive the kinetic energy from the momentum distribution by

$$\langle p^2\rangle = \int x(\mathbf{p})x^*(\mathbf{p})p^2\mathbf{dp} \tag{19}$$

or

$$\langle p^2\rangle = \int_0^\infty I(p)p^2 dp \,. \tag{20}$$

It has been demonstrated by Ibers (1958) that the structure factor for fast electron scattering is related to $\langle r^2\rangle$ for the zero value of the scattering parameter $q$ and so it can give information on the diamagnetic susceptibility.

It was also shown by Cornille (1966), that in the momentum space, the value of the profile $J(q')$ for the zero value of the parameter $q'$ gives the mean value $\langle p^{-1}\rangle$.

In general it is possible to say that the scattered intensities and Compton profiles may give informations about some of $\langle r^n\rangle$ and $\langle p^n\rangle$.

Concerning the shape of the energy distributions, they could provide a point comparison for various theoretical calculations and experiments of high accuracy.

As the aim of this paper is not to study the accuracy of the calculations but rather to show that the scattering effects can provide interesting and useful information about electron charge distributions, we will only discuss a typical case for one atom and one molecule.

## Details of the calculations

Equations (9) and (10) have been used to calculate the total and coherent intensities for incident beams of X-rays and equations (11), (12) and (13) to calculate the total and elastic intensities in the case of fast electrons and to compute the Compton profiles, with various wave functions for certain atoms and molecules.

### (*a*) *Atoms*

For the atoms from Li to Ne, four types of scattered intensities and the Compton profiles have been calculated with the use of wave functions from Slater (1930), Duncanson & Coulson (1944), Clementi, Roothaan & Yoshimine (1962), and in the case of Ne with wave functions calculated by Sachs (1961), Roothaan (1951), Donath (1961), and Bernal & Boys (1952).

The most typical case of the Ne atom has been chosen for discussion here.

### (*b*) *Molecules*

Molecular calculations, as is well known, are more difficult than atomic calculations, owing to the complexity of various polycentric integrals, so these calculations of scattering effects were first studied with the help of the atomic formalism, for certain molecules for which there are one-centre molecular wave functions computed in the united atom approximation particularly for $CH_4$, $NH_3$, HF and $H_2O$ by Moccia (1964).

The case of the $NH_3$ molecule was selected for discussion here.

## Discussion

### (*a*) *Atoms*

Table 1 gives the results obtained for the Ne atom with various wave functions including: the width of the Compton profile $\Delta I$; the values of $\langle r^2\rangle$ from Dawson's (1961) work, the values of $\langle p^{-1}\rangle$ deduced by Cornille (1966) from the Compton profiles for $q'=0$ and the total energies. The results are divided in two groups placed to the right and to the left of the experimental values, for $\langle r^2\rangle$ and for $\Delta I$. Although the uncertainties in the experimental values, especially for $\langle r^2\rangle$, are considerable, it seems that they can be put in the same column as the experimental energies and the experimental value of the Compton profile width, for comparison. We can deduce from Table 1 that, when plotted against the widths $\Delta I$, the total energies (which have the same magnitude as the kinetic energy but the opposite sign, if the virial theorem is satisfied) are seen to pass through a minimum; the minimum for the energy must correspond to the experimental energy or kinetic energy, so the value of $\langle p^2\rangle$ which corresponds to the minimal energy value must in turn correspond to the best value of $\Delta I$. It appears also from

Table 1. *Compton profile widths, $\Delta l$, mean values for $\langle r^2 \rangle$ and $\langle p^{-1} \rangle$, and total energies for the* Ne *atom*

| Wave functions | Slater | Duncanson & Coulson | Roothaan | $E_x$ | Donath P.D. | Bernal & Boys P.D. | H-F. Sachs, Clementi, Donath | Hartree | Boys R.F. | Thomas, Fermi, Dirac | Thomas, Fermi |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\Delta l_{ux}$ | 33·88 | 33·88 | 33·88 | 32 | 28·82 | 28·72 | 28·61 | 28 | 26·90 | | 3 |
| $\langle r^2 \rangle_{\text{u.a.}}$ | 7·16 | 7·33 | | 9·10 | | 9·15 | 9·41 | | 9·20 | 19·07 | |
| $\langle 1/p \rangle_{\text{u.a.}}$ | 4·87 | 4·92 | 4·95 | | 5·33 | 5·46 | 5·45 | | 5·61 | | |
| $E_{\text{tot u.a.}}$ | −127·799540 | | −127·81219 | −129·03 | −128·740 00 | −128·690 00 | −128·5470 00 | | −128·14 | | |

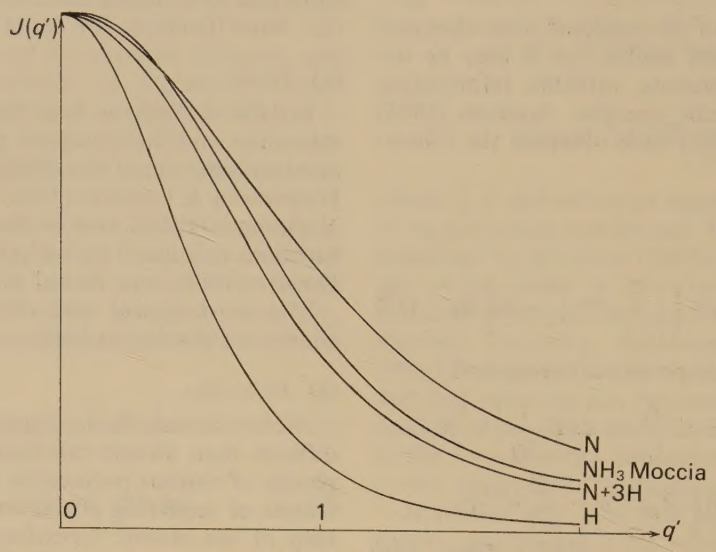


Fig. 1. Compton profile calculation for: N, H, N+3H, calculated with Clementi (1963) wave functions, and for $NH_3$ molecule with the Moccia (1964) wave function.

Table 1 that the data are internally consistent in so far as a large value of $\Delta l$ corresponds to a small value of $\langle r^2 \rangle$; a large value of $\langle r^2 \rangle$ corresponds to a large value of $\langle p^{-1} \rangle$.

The various relationships between $\Delta l$ and $\langle r^2 \rangle$, $\langle p^{-1} \rangle$ and $\langle r^2 \rangle$ and $\langle p^2 \rangle$ and $\Delta l$ are in agreement with what could be expected from the uncertainty principle.

All these results agree well with the known radial characteristics of the Hartree–Fock and Slater wave functions and suggest that the Slater radial densities are too contracted and the Hartree–Fock radial densities too dispersed.

Table 2 gives the same information for the listed structure factors; it can be seen that the results, here

Table 2. *X-ray scattering factor for the* Ne *atom, calculated with various wave functions*

| $\sin \frac{1}{2}\theta/\lambda$ (Å$^{-1}$) | $f$ (Slater) | $f$ (D.C.) | $f$ (P.D.R.F.) | $f$ (H.F.) |
|---|---|---|---|---|
| 0·00 | 10·00 | 10·00 | 10·00 | 10·00 |
| 0·10 | 9·48 | 9·36 | 9·359 | 9·351 |
| 0·20 | 8·15 | 8·00 | 7·812 | 7·808 |
| 0·30 | 6·52 | 6·40 | 6·070 | 6·084 |
| 0·40 | 4·90 | 4·80 | 4·599 | 4·617 |
| 0·50 | 3·66 | 3·65 | 3·520 | 3·530 |
| 0·60 | 2·82 | 2·80 | 2·782 | 2·782 |
| 0·70 | 2·32 | 2·30 | 2·295 | 2·288 |
| 0·80 | 2·00 | 1·99 | 1·975 | 1·965 |
| 0·90 | 1·78 | 1·75 | 1·765 | 1·752 |
| 1·00 | 1·61 | 1·60 | 1·621 | 1·608 |

again, fall into two groups. A similar division was also obtained by Cornille (1966) for the coherent and total intensities of X-ray scattering and for the elastic and total intensities of fast electron scattering.

(*b*) *Molecules*

The study of molecular electronic densities is relevant to the chemical bonding. For this reason, the four types of scattered intensities and the Compton profiles were calculated for $CH_4$, $NH_3$, $OH_2$ and HF. We will discuss only the case of the ammonia molecule. These calculations have been done with the single-centre expansion wave functions which permit the use of the much simpler atomic formalism. Some results are given in Figs. 1 and 2.

Fig. 1 gives the Compton profiles respectively obtained for the N and H atoms, N+3H atoms and $NH_3$ molecule calculated with the Moccia (1964) wave function. The curves show that for the molecular profile, $\Delta l$ is larger than the one obtained with the sum of the atomic profiles, a result which is compatible with the hypothesis that a contraction of electronic densities occurs when a chemical bond is formed. This hypothesis is strengthened by comparing these results with those of Fig. 2, which gives as an example the elastic-scattered intensities multiplied by $q^2$ for the ammonia molecule, for the Debye and Ehrenfest model which

does not take into account the effect of the chemical bond (curve *A*), the molecular calculation with Moccia wave function (curve *B*) and the sum of the atomic contributions (dotted line). It can be seen that the results of the *A* and *B* calculations are quite different for small values of the diffraction parameter $q$. The difference was attributed to the effect of chemical bonding, which produces a contraction of the electronic density; these results have been confirmed by Tavard (1966) using polycentric wave functions and structure factors and also, experimentally, by Bonham & Iijima (1963) and Rouault & Gervais (1966).

Table 3 gives the most probable value of the momentum $p_m$ which is not very different from the mean momentum $\langle p \rangle$ in the molecules (Sears, 1959). The comparison for two isoelectronic sequences of molecules between $p_m$, total energies and equilibrium distances shows that variations observed in the most probable $p_m$ correlate with the variations of the internuclear distances. This indicates a contraction of the electronic densities from $CH_4$ to HF and from $SiH_4$ to HCl. The mean value $\langle p \rangle$ must be the only quantity used when comparing the difference between the molecule and the sum of the atoms.

## Conclusion

The curves giving the scattered intensities and the shapes of the Compton profiles, from which the kinetic and potential energy distributions may be inferred as well as informations about some $\langle r^n \rangle$ and $\langle p^n \rangle$, are relevant to very recent work of Tong & Sham (1966) and Cowan, Larson, Liberman, Mann & Waber (1966) on scattering, and to the work of Smith & Richardson (1965), Robinson (1965), Rosenfeld (1964), Bader (1964), Bader & Henneker (1965) and Ransil (1966), on electronic densities, density differences, and discussions related to the problem of chemical bonding.

Unfortunately, if there are some very accurate experiments on scattering available, there are only very old determinations of Compton profiles. Only two recent investigations have been carried out on the profiles of lithium and graphite, namely by Cooper, Leake & Weiss (1965) and by Cooper & Leake (1966), and the authors would be interested to learn of further experiments, if any have been carried out, on light gaseous atoms or molecules.

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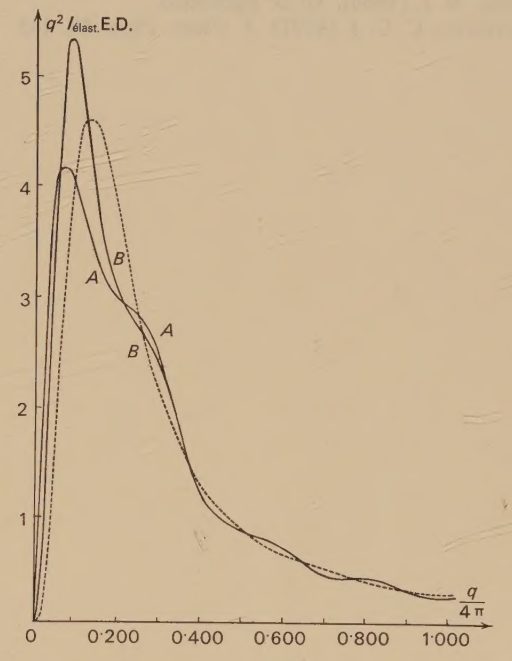


Fig. 2. Elastic-scattered intensities multiplied by $q^2$, calculated, curve *A*: with the Debye and Ehrenfest model, curve *B*: with the molecular Moccia (1964) wave function. Dotted lines: atomic contributions.

Table 3. *Equilibrium distances, total energies and most probable momentun for two sets of isoelectronic molecules*

All calculations done with Moccia (1964) wave functions

| | $CH_4$ | $NH_3$ | $H_2O$ | HF |
|---|---|---|---|---|
| $R_e$ (Bohr) | 2·067 | 1·912 | 1·810 | 1·73 |
| $E$ (Hartree) | −40·5 | −56·58 | −76·46 | −100·48 |
| $p_m$ (a.u.) | 0·84 | 0·91 | 1·05 | 1·21 |
| | $SiH_4$ | $PH_3$ | $SH_2$ | ClH |
| $R_e$ (Bohr) | 2·76 | 2·68 | 2·52 | 2·41 |
| $E$ (Hartree) | −292·141 | −343·42 | −400·81 | −462·81 |
| $p_m$ (a.u.) | 0·66 | 0·73 | 0·86 | 0·94 |

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